424. cyclo*Hexane Derivatives. Part II.** *The Mechanism of Catalytic Hydrogenation of Cyclic Compounds.*

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The factors controlling the stereoisomeric compositions of the products obtained by catalytic hydrogenation of substituted *cyclo*hexanones and phenols have been studied, and the use of the Skita rule for predicting these compositions has been found to be misleading. *cis-trans*-Isomerisation of substituted *cyclo*hexanols in the presence of alkaline hydrogenation catalysts has been established as a general reaction, and some of the factors controlling it have been elucidated.

The factors influencing the proportion of *cis-trans*-isomers obtained on hydrogenation of substituted *cyclo*hexanones or phenols have not been fully elucidated. The present work aimed at establishing these with more certainty and testing the validity of the Skita rule.

Extensive studies by Skita in the 1920's led to his rule, that reductions in acid solvents lead to products rich in *cis*-isomer, whereas those in neutral or alkaline solvents lead to products rich in *trans*-isomer. The general applicability of the rule has been discussed by Weidlich,[1, 2] who considered that acid or alkali causes a change in the mode of addition of hydrogen by controlling in some way the " polar character " of the molecule; but the exact meaning of the term " polarity " as used by Weidlich is not at all clear. Rate of hydrogenation has also been thought to be a factor, rapid hydrogenation being considered to lead to products rich in the *cis*-form and slow hydrogenation to products rich in *trans*-form.[3, 4] There are also many references to the effect of the activity of the catalyst and Skita later considered the temperature, hydrogen pressure, and catalyst activity all to be factors controlling the proportion of stereoisomers produced.[4] For αβ-unsaturated ketones the effects of acid and alkali have been related to enol formation and subsequent effect on the course of hydrogenation;[2, 5] different types of catalyst have also been considered to affect the stereoisomer ratios.[6a] A mechanism has also been suggested by Brewster [6b] to explain the effects observed by Skita.

The above position is further confused by the fact that until recently it has always been assumed that the *trans*- is more stable than the *cis*-isomers of 2-, 3-, or 4-substituted *cyclo*hexanols, and many of the above generalisations were formulated by means of *cis-trans*-terminology. In 1947, however, Hassel, and Pitzer and others showed that for 3-substituted *cyclo*hexanes the *cis*- is the more stable isomer. The difficulty then arises whether the Skita rule should be stated in terms of the stability or the configurations of the isomers. The former view should presumably be taken.

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* Part I, *J.*, 1955, 3122.

[1] Weidlich, " Handbuch der Katalyse," Ed. Schwab, Springer, Vienna, 1943, Vol. VII, p. 755.

[2] *Idem, Chemie*, 1945, **58**, 30.

[3] Ott and Schröter, *Ber.*, 1927, **60**, 624.

[4] Skita and Faust, *Ber.*, 1931, **64**, 2878.

[5] Badin and Pacsu, *J. Amer. Chem. Soc.*, 1944, **66**, 1963.

[6] (*a*) Brode and Van Dolah, *Ind. Eng. Chem.*, 1947, **39**, 1157; (*b*) Brewster, *J. Amer. Chem. Soc.*, 1954, **76**, 6361.

The Skita rule has been modified and reformulated in terms of modern conformational analysis by Barton,[7] who also discusses the effect of hydrogenation rate and the steric effects of any hindering groups in the ketone on the final conformation of the products.

The experimental work on which the above generalisations are founded is far from satisfactory. A critical survey of Skita's work [8, 9] shows that in many cases there are no details of the yields or the methods used in determining the isomeric composition of the products, which are merely stated to be " rich " in one or other isomer. In later work Skita [4] used refractive index and density as a means of determining *cis*–trans-composition, and showed that his earlier isomers were impure; but more recent work has shown that even some of his later compounds are not the pure isomers as shown by their refractive indices (see Table 1) and densities.

Gough, Hunter, and Kenyon [10] based their analysis on viscosities, but some of their isomers were impure as is shown by their refractive indices (see Table 1) and densities. Since that time considerable work has been reported, especially by Cornubert, Vavon, Mousseron, and their co-workers, but the validity of the method used by these workers, namely, the conversion into solid esters followed by fractional crystallisation and thermal analysis of the ester fractions, is not really reliable since very poor material balances were obtained (see Peppiatt and Wicker [14]). Brode and van Dolah's work [6] is based on the incorrect refractive indices given by Skita and Faust.[4]

TABLE 1. *Refractive indices of the methyl*cyclo*hexanols at* 20°.

ortho		*meta*		para		Ref.
cis	*trans*	*cis*	*trans*	*cis*	*trans*	
1·4623	1·4590	1·458	1·455	1·4592	1·4586	9
1·4640	1·4611	1·4550	1·4572	1·4549	1·4586	4
1·4616	1·4596	1·4554	1·4530	1·4584	1·4544	10
1·4649 *	1·4616 *	1·4573 *	1·4583 *	1·4616 *	1·4561 *	11, 12
1·4641 *	1·4611 *					13

* Authentic values.

The most reliable method of analysis is one based on physical properties of the total product in which the values of the two stereoisomers concerned show a reasonably measurable difference. Differences in refractive indices are usually small, but in the case of the methyl*cyclo*hexanols density differences are quite appreciable and have been used by Macbeth and his co-workers,[11, 12] and also in the present work. Another such method is one based on melting point–composition diagrams, conveniently where both stereoisomers are solids, as is the case with 4-*cyclo*hexyl- and 3 : 3 : 5-trimethyl-*cyclo*hexanol, which have also been used in the present work. All these compounds were selected for study because their configuration is beyond doubt.

cis-Addition of hydrogen to double bonds (*i.e.*, from the same side of the bond) would be expected [15] and has been assumed in many discussions of the mechanism of hydrogenation in the literature. The difficulty arises as to how to account then for the presence of isomers. Some workers have suggested that in these cases some hydrogenation mechanism other than *cis*-addition occurs.[16] Others [15] suggest subsequent isomerisation but the evidence for this is very scant. Kuhn [17] states that platinum catalysts can cause isomerisation but gives no details; Loew and Aso [18] obtained a 10·5% conversion of maleic into fumaric

[7] Barton, *J.*, 1953, 1027, footnote 23.
[8] Skita, *Annalen*, 1922, **427**, 255.
[9] *Idem, ibid.*, 1923, **431**, 1, and many later papers.
[10] Gough, Hunter, and Kenyon, *J.*, 1926, 2052.
[11] Jackman, Macbeth, and Mills, *J.*, 1949, 1717.
[12] Macbeth and Mills, *J.*, 1945, 709.
[13] Arnold, Smith, and Dodson, *J. Org. Chem.*, 1950, **15**, 1256.
[14] Peppiatt and Wicker, *Chem. and Ind.*, 1955, 747.
[15] Farkas and Farkas, *Trans. Faraday Soc.*, 1937, **33**, 837 and other papers.
[16] Linstead, Doering, Davis, Levine, and Whetstone, *J. Amer. Chem. Soc.*, 1942, **64**, 1955.
[17] Kuhn in Freudenberg's " Stereochemie," Deuticke, Leipzig, 1932, Vol. II, p. 918.
[18] Loew and Aso, *Bull. Coll. Agric. Tokyo Imp. Univ.*, 1906, **7**, 1–6.

acid with platinum black and water, and Zelinski and Margolis[19] found that *cis*-1 : 2-dimethyl*cyclo*hexane was partly isomerised to the *trans*-isomer when the vapour was passed over a nickel catalyst.

It has now been found that the isomerisation which occurs when 3 : 3 : 5-trimethyl*cyclo*hexanol is heated with a nickel catalyst, reported in Part I, is a general reaction, and that substituted *cyclo*hexanols in general can be isomerised by heating them with hydrogenation catalysts such as nickel or platinum, in an atmosphere of hydrogen. If sufficient catalyst is used (*e.g.*, 50%) isomerisation can be brought about at room temperature. The isomerisation presumably leads eventually to equilibrium mixtures of the two isomers. Table 2 shows the results obtained with 3 : 3 : 5-trimethyl-, 4-*cyclo*hexyl-, and 3-methyl-*cyclo*hexanol. It can be seen that the equilibrium position is largely independent of temperature in the range examined, but temperature, catalyst concentration, and presumably catalyst activity all affect the rate of attainment of equilibrium.

TABLE 2. *Isomerisation with a nickel catalyst.*

Compound	Temp.	Catalyst	(%)	Reaction time (hr.)	Stable isomer (%) in product
trans-3 : 3 : 5-Trimethyl*cyclo*hexanol	20°	Ni	50	18	72 (*cis*)
,, ,, ,,	85	,,	2·5	66	76 ,,
,, ,, ,,	110	,,	2·5	16	76 ,,
,, ,, ,,	130	,,	2·5	9	70 ,,
,, ,, ,,	130	,,	2	5	76 ,,
cis- ,, ,, ,,	140	,,	2·5	9	73 ,,
trans-4-*cyclo*Hexyl*cyclo*hexanol	130	,,	5	5	41—49 (*trans*)
,, ,, ,, ...	180	Pt	5	5	49 (*trans*)
3-Methyl*cyclo*hexanol (32% *cis*)	160	Ni	2·5	5	83 (*cis*)

Alkali was found to be essential for the isomerisation. A nickel catalyst, whether Raney nickel or reduced nickel, is alkaline, and it has been shown recently that Adams platinum catalyst also contains alkali:[20] we found that this also caused isomerisation, for example, of *trans*-4-*cyclo*hexyl*cyclo*hexanol (see Table 2). However, if the platinum catalyst has been used in acid solution it is necessary to add alkali before isomerisation can be brought about For example, *trans*-3 : 3 : 5-trimethyl*cyclo*hexanol could not be isomerised with acid-washed platinum but was readily isomerised when a little sodium carbonate was added. Sodium carbonate without a catalyst would not isomerise the starting material. These facts suggested that the effect of acid and alkali on the stereoisomerism of the products of hydrogenation suggested by Skita, on which he based his rule, might be explained by the fact that subsequent isomerisation tends to give the more stable product when alkali is used. We therefore studied the effects of acid and alkali on the proportions of isomers produced from substituted *cyclo*hexanones under conditions where isomerisation would be small, *i.e.*, with nickel or platinum at room temperature. Table 3 shows the results, together with those of earlier work where the isomer analysis is beyond doubt. Reductions of phenols are also included, although in these cases the reaction cannot be carried out at room temperature with nickel catalyst. This Table shows that for 2-methyl-*cyclo*hexanone acid and alkali have little effect, but for 3-methyl*cyclo*hexanone, dihydro-*iso*phorone, and 4-*cyclo*hexyl*cyclo*hexanone a greater proportion of the more stable isomer results from reduction in acid than in alkaline media which is contrary to the Skita rule. For 4-methyl*cyclo*hexanone the results with platinum conform to the rule, but that with nickel does not. The effect of acid and alkali on the reduction is therefore not as simple as is suggested by the Skita rule.

It will be seen that reduction with nickel gave more of the stable isomer at high temperatures than at room temperature. This is to be expected, since the presence of alkali in nickel results in isomerisation if the reaction is carried out at a sufficiently high temperature.

The following theory, based essentially on postulates of Farkas and Farkas,[15] Linstead,[16] and Seigal,[21] is suggested. Hydrogenation is assumed to occur by *cis*-addition to the double

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[19] Zelinski and Margolis, *Ber.*, 1932, **65**, 1613; Margolis, *Ber.*, 1936, **69**, 1710.

[20] Kennan, Giesemann, and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 229.

[21] Seigal, *ibid.*, 1953, **75**, 1317.

bond and will add preferentially to the more accessible side of the double bond, *i.e.*, that side which presents the least steric hindrance to absorption on the catalyst.

Consider the substituted *cyclo*hexanones (see Fig. 1). The chair form with an equatorial group R will be absorbed preferentially on the catalyst as shown, in the least hindered position, addition of hydrogen being to the least hindered side of the $>$C=O linkage, *i.e.*, to the equatorially placed π electron streamer 2, leading to the formation of an axial hydroxyl group. In a preliminary report,[14] which was instigated by Cornubert's paper,[22]

TABLE 3. *Proportions of isomers produced by catalytic hydrogenation of substituted* cyclo*hexanones and phenols.*

Compound reduced	Catalyst	Solvent	Temp.	Stable isomers (%) in product	Ref.
2-Methyl*cyclo*hexanone	Pt	AcOH	20°	30 *trans*	†
,, ,,	Ni	—	20	34 ,,	†
,, ,,	Ni	—	130	43 ,,	11
3-Methyl*cyclo*hexanone	Pt	AcOH	20	73 *cis*	†
,, ,,	Ni	—	20	23 ,,	†*
,, ,,	Ni	EtOH	140	23 ,,	12
,, ,,	Ni	—	160	56 ,,	†*
4-Methyl*cyclo*hexanone	Pt	AcOH	20	53 *trans*	†
,, ,,	Pt	MeOH	20	74 ,,	†
,, ,,	Ni	—	120—130	41 ,,	11
Dihydro*iso*phorone	Ni	MeOH	20	12 *cis*	†
,, ,,	Ni	—	130	73 ,,	†
,, ,,	Pt	MeOH	20	9 ,,	†
,, ,,	Pt	AcOH	20	17 ,,	†
,, ,,	Pt	MeOH–C_6H_{11}·NMe_2	20	10 ,,	†
4-*cyclo*Hexyl*cyclo*hexanone	Ni	MeOH	20	15—20 *trans*	†
,, ,,	Pt	AcOH	20	46 ,,	†
,, ,,	Pt	MeOH	20	45 ,,	†
3 : 3 : 5-Trimethyl*cyclo*hex-2-en-1-ol	Ni	,,	20	20 *cis*	†
o-Cresol	Ni	—	160	73 *trans*	†
,,	Pt	AcOH	25	0 ,,	*a*
,,	Ni	—	180	68	11
m-Cresol	Ni	EtOH	200	85 *cis*	12
,,	Ni	—	160	55 ,,	†
,,	Ni	—	160	83 ,,	†
			(extra 5 hrs. isomerisation)		
p-Cresol	Ni	—	180	82 *trans*	11
,,	Ni	—	160	63 ,,	†

* For details see Part I. † Present work.
(*a*) Baker and Schuetz, *J. Amer. Chem. Soc.*, 1947, **69**, 1250.

TABLE 4.

Compound	Conformation *	Expected preponderant isomer
2-Methyl*cyclo*hexanone	e chair	*cis*
,, ,,	a chair	Approx. equal but larger alkyl groups give *cis*
,, ,,	1 : 2 enol	*cis* (only)
,, ,,	5 : 6 enol	Approx. equal
3-Methyl*cyclo*hexanone	e chair	*trans*
,, ,,	a chair	*cis*
,, ,,	1 : 2 enol	Approx. equal
,, ,,	5 : 6 enol e-Me	Approx. equal
,, ,,	5 : 6 enol a-Me	*cis*
4-Methyl*cyclo*hexanone	e chair	*cis*
,, ,,	a chair	*trans*
,, ,,	enol e-Me	Approx. equal
,, ,,	enol a-Me	*cis*
Dihydro*iso*phorone	e chair	*trans*
,, ,,	a chair (v. unstable)	*cis*
,, ,,	1 : 2 enol e-Me	Approx. equal
,, ,,	1 : 2 enol a-Me	*cis*
,, ,,	5 : 6 enol quasi-e-Me	Approx. equal
,, ,,	5 : 6 enol quasi-a-Me	*cis*

* a = axial. e = equatorial. See Barton, Cookson, Klyne, and Shoppee, *Chem. and Ind.*, 1954, 21, for definition of quasi-forms.

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[22] Cornubert, Barraud, Cormier, Descharmes, and Eggert, *Bull. Soc. chim. France*, 1955, 400.

only the forms with an equatorial alkyl group were considered. Similar consideration of the form with an axial alkyl group shows that an axial hydroxyl group is still formed but in this case the product, the axial-axial alcohol, will rapidly pass into the more stable equatorial-equatorial form. When one also considers the enolic forms of the ketone, which are known to be present in *cyclo*hexanones,[23] the examination of models by the above method leads to the results shown in Table 4. Thus the isomeric composition of the products will depend on the proportions of the various types of isomer present in the ketone. For substituted *cyclo*hexanes the chair-equatorial are more stable than the chair-axial conformations at room temperature, but little is known of the *cyclo*hexanones and here axial forms may make a substantial contribution: α-halogeno*cyclo*hexanones for example, have been shown to exist entirely in the chair-axial form.[24]

FIG. 1.

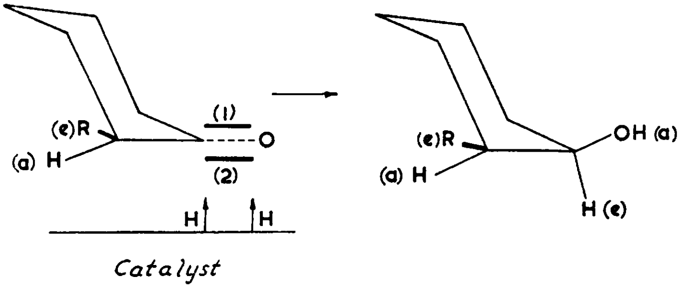
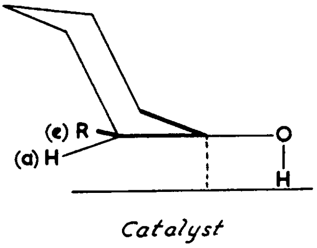


FIG. 2.



Alkali and acid will affect the proportions of enol and keto-forms and thus may change the proportion of stereoisomers produced in hydrogenation. Prediction of the stereoisomeric composition of the products of catalytic hydrogenation is therefore impossible unless the conformational and tautomeric composition of the ketone is known.

The well-known tendency of 2-alkyl*cyclo*hexanones to yield mainly the *cis*-alcohol whatever the solvent is readily explained by Table 4, and the tendency of dihydro*iso*phorone to give mainly the *trans*-alcohol is understandable since the axial-chair form of the ketone shows strong interaction and would be very unstable, and examination of the equatorial-chair form shows that hydrogenation would lead mainly to the *trans*-alcohol, alkali causing a slight shift towards the *cis*-isomer.

The occurrence of isomerisation at high temperatures in the presence of catalyst and alkali can be explained as follows. Hydrogenation catalysts can also dehydrogenate alcohols to ketones, and an alcohol in the presence of such a catalyst will afford the following equilibrium:

$$trans\text{-Alcohol} \rightleftharpoons \text{Ketone (e-alkyl)} \rightleftharpoons \text{Ketone (a-alkyl)} \rightleftharpoons cis\text{-Alcohol.}$$

Increase of temperature, catalyst concentration, catalyst activity, and reaction time all favour production of the isomer which is stable at the reaction temperature.

Isomerisation by redistribution of bonds in the half-hydrogenated state, as suggested by Polyani and Greenhalgh[25] for alkenes, is not applicable in the present case, since the bonds to be redistributed form part of a *cyclo*hexane ring (see Fig. 2, the bonds referred to are in heavy print).

The function of alkali in the isomerisation process is probably that of a catalyst modifier since we have established that platinum containing alkali (*i.e.*, Adams catalyst) is an effective dehydrogenation catalyst, whereas platinum which has been acid-washed is very inefficient for dehydrogenation; therefore when acid-washed platinum is used dehydrogenation is slow and so isomerisation is slow. Hydrogenation with Adams platinum is slow[20] and the tendency of the operator would be to increase the temperature in such cases and possibly promote isomerisation. On the other hand, if acid solvents are used

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[23] Schwarzenbach and Wittwer, *Helv. Chim. Acta*, 1947, **30**, 669.
[24] Corey, *J. Amer. Chem. Soc.*, 1953, **75**, 2301.
[25] Greenhalgh and Polanyi, *Trans. Faraday Soc.*, 1939, **35**, 520.

with platinum, or if the platinum has been previously used in acid media, the alkali in the catalyst is neutralised so that isomerisation does not occur. The use of a nickel catalyst with phenols is limited to temperatures of about 160° or more and thus some isomerisation will always occur. Hydrogenations at elevated temperatures may lead to mixtures rich in the stable isomer even in the absence of alkali, since the equilibrium of the ketone may be shifted towards forms which on hydrogenation give the stable alcohol. Hydrogenation being far faster than dehydrogenation at room temperature, isomerisation does not take place measurably at that temperature, providing that normal amounts (*e.g.*, up to 5—10%) of catalyst of average activity are used. Even at elevated temperatures or with very large amounts of catalyst it is possible to hydrogenate *iso*phorone to products containing high percentages of *trans*-alcohol provided the reaction is stopped before isomerisation has proceeded to an appreciable extent (see Table 5).

TABLE 5. *Hydrogenation of* iso*phorone to* 3 : 3 : 5-*trimethyl*cyclo*hexanol.*

Temp.	Ni catalyst (%)	Time (hr.)	*trans*-Isomer (%)	Ketone (%) in product	Temp.	Ni catalyst (%)	Time (hr.)	*trans*-Isomer (%)	Ketone (%) in product
20	2·5	18	83	0	90	2·5	0·22	82	3·5
50	2·5	23	81	,,	100	2·5	0·3	73	1·5
55	2·5	44	80	,,	110	1	0·22	76	8
75	2·5	16	82	,,	155	0·5	16	~50	11
85	2·5	20	75	,,	180	0·5	3·5	~50	13

Reduction of substituted phenols under conditions where isomerisation of the *cyclo*hexanols produced can occur will proceed similarly to that of substituted *cyclo*hexanones under similar conditions. However, reduction of substituted phenols or disubstituted benzenes generally, at room temperature with, *e.g.*, platinum in acid, may follow a different pattern. The proportion of stereoisomers produced depends on whether the planar benzene nucleus is reduced by simultaneous addition of six hydrogen atoms, in which case *cis*-isomers will be invariably produced, or whether the reduction is stepwise, in which case the ultimate step will be addition to a quasi-chair type of compound producing mixtures of isomers.

The only example in Table **3** of a substituted phenol reduced at room temperature with platinum is *o*-cresol which gives pure *cis*-2-methyl*cyclo*hexanol. However, reductions of dialkylbenzenes with platinum at room temperature appear to give mixtures (see, *e.g.*, Baker and Schuetz;[26] Mousseron[27]).

EXPERIMENTAL

M. p.s of the hydrogenation products were determined by a standard cooling-curve method. Other m. p.s were determined by the capillary method. Unless otherwise stated, light petroleum refers to material of b. p. 60—80°.

The *iso*phorone was purified as described in Part I. The three methyl*cyclo*hexanones were obtained by chromic oxide–acetic acid oxidation of the corresponding alcohols. *cis–trans*-Compositions were determined by thermal analysis in the case of 3 : 3 : 5-trimethyl*cyclo*hexanol (for m. p.–composition values see Part I) and 4-*cyclo*hexyl*cyclo*hexanol, and by density measurements for the three methyl*cyclo*hexanols, the values given by Jackman, Macbeth, and Mills[11] and Macbeth and Mills[12] being used for the pure stereoisomers. Ketone was assayed by the hydroxylamine method. Hydrogenations were usually complete but corrections were made for any unhydrogenated ketone.

Preparation of trans-4-cyclo*Hexyl*cyclo*hexanol.*—*p*-*cyclo*Hexylphenol (704 g., 4 mole) was hydrogenated with a reduced nickel catalyst (20 g.) at 160—180°/100 lb. per sq. in. The catalyst was filtered off and the product solidified (m. p. ~80°). This product was subjected to systematic fractional crystallisation from acetone, to give 140 g. of product, m. p. 102—103°; further recrystallisation from ethylene dichloride at 0° gave *trans*-4-*cyclo*hexyl*cyclo*hexanol (108 g.; m. p. 103·5°). Recrystallisation from light petroleum gave *trans*-4-*cyclo*hexyl*cyclo*hexanol of high purity, as indicated by its cooling curve, and suitable for determination of the m. p.–composition diagram.

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[26] See ref. (*a*), Table 3.

[27] Mousseron, *Bull. Soc. chim. France*, **1946** 218.

Preparation of cis-4-cyclo*Hexyl*cyclo*hexanol.*—4-*cyclo*Hexyl*cyclo*hexanone (44 g.), dissolved in methanol (20 ml.), was hydrogenated with a reduced nickel catalyst (1·25 g.) at room temperature/100 lb. (16 hr.). The recovered product crystallised (42 g.; m. p. ~80°) and was heated with 3 : 5-dinitrobenzoyl chloride (58 g.) at 160° for 30 min. The solid product was triturated twice with saturated sodium hydrogen carbonate solution, filtered off, and washed with water, and recrystallised in turn from acetic acid, acetone, then light petroleum containing a little acetone, to give *cis*-4-*cyclo*hexyl*cyclo*hexyl dinitrobenzoate (27 g.; m. p. 162—163°). The ester (25 g.) was then hydrolysed with potassium hydroxide (7 g.) in water (50 ml.) and alcohol (500 ml.) and worked up in the normal way, to give 4-*cyclo*hexyl*cyclo*hexanol (11 g.; m. p. 85—93°). Vacuum-distillation gave 9·05 g. of product, b. p. 130—140°/1·5 mm., m. p. 90—94°. Recrystallisation three times from light petroleum and once from light petroleum (b. p. 40—60°) gave *cis*-4-*cyclo*hexyl*cyclo*hexanol (7·4 g.; m. p. 92·5°) of high purity as indicated by its cooling curve.

Melting Point–Composition Curve.—This was constructed for 4-*cyclo*hexyl*cyclo*hexanol and used as described for 3 : 3 : 5-trimethyl*cyclo*hexanol in Part I, with the following results :

trans (%)	100	90	85	80	70	60	50	40	30	20	10	5	0
M. p. ...	103·5°	98·5°	95·6°	94·0°	94·4°	94·0°	91·8°	88·5°	84·0°	82·0°	88·5°	90·5°	92·5°

The correction to the m. p. of 4-*cyclo*hexyl*cyclo*hexanol was 0·6° per 1% of 4-*cyclo*hexyl*cyclo*hexanone present.

Preparation of 4-cyclo*Hexyl*cyclo*hexanone.*—4-*cyclo*Hexyl*cyclo*hexanol (*cis*- and *trans*-mixture 250 g.) was oxidised with chromic trioxide–acetic acid by the method of Shunk and Wilds,[28] giving crude ketone (226 g., 90%), which was then fractionated to give 4-*cyclo*hexyl*cyclo*hexanone (160 g.), m. p. 30·5°.

*Preparation of Dihydro*iso*phorone.*—*iso*Phorone (690 g., 5 mole) was hydrogenated with a reduced nickel catalyst (20 g.) at 90°/100 lb. until the theoretical amount of hydrogen had been taken up. Catalyst was removed by filtration. The product containing 88% of dihydro*iso*phorone and 7% of *iso*phorone was distilled, the fraction of b. p. 120—121°/100 mm., n_{D}^{20} 1·4450—1·4452, being collected. Ketone assay by the hydroxylamine method indicated 99—100% purity.

Preparation of 3 : 5 : 5-*Trimethyl*cyclo*hex*-2-*enol.*—Lithium aluminium hydride (3 g.) in anhydrous ether (300 ml.) was slowly added to a stirred solution of *iso*phorone (10 g.) in anhydrous ether (100 ml.) at −10° in an ice-bath, the temperature being kept below 10°. Stirring was continued for a further 15 min. Excess of reagent was destroyed with water, the precipitated solids were dissolved by the addition of dilute sulphuric acid, and the ether layer was separated, washed with water, dried (Na_2SO_4), and evaporated. The residue was distilled, to give 3 : 5 : 5-trimethyl*cyclo*hex-2-enol (7·5 g., 75%) containing 1·7% of *iso*phorone.

Pressure Hydrogenation.—The compound to be reduced with the stated amount of reduced nickel catalyst was hydrogenated at 100 lb. at the temperature given. Methanol was used as a solvent when compounds were solid at the working temperature. The catalyst was removed by filtration, and any solvent by distillation. The product was then completely distilled and analysed by either density or thermal methods. The following compounds were reduced by this method with the results given.

(1) Dihydro*iso*phorone (14 g., 0·1 mole), catalyst (0·3 g.), methanol (15 ml.), 20°/16 hr. Product : m. p. 54°, contained 12% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(2) *iso*Phorone (10 g.), catalyst (0·25 g.), methanol (10 ml.), 75°/16 hr. Product : m. p. 50·3° (ketone absent), contained 18% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(3) *iso*Phorone (20 g.), catalyst (0·50 g.), 90°/13 min. Product : m. p. 47·8° (containing 3·5% of dihydro*iso*phorone), contained 18% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(4) *iso*Phorone (56 g.), catalyst (1·4 g.), 100°/18 min. Product : m. p. 42·5° (containing 1·7% of dihydro*iso*phorone), contained 27% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(5) *iso*Phorone (20 g.), catalyst (0·2 g.), 110°/13 min. Product : m. p. 39·6° (containing 8% of dihydro*iso*phorone), contained 24% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(6) *iso*Phorone (56 g.), catalyst (0·28 g.), 180°/3·5 hr. Product : m. p. 7° (containing 13% of dihydro*iso*phorone), contained *ca.* 50% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(7) *iso*Phorone (56 g.), catalyst (0·28 g.), 155°/16 hr. Product : m. p. 15° (containing 11% of dihydro*iso*phorone), contained approx. 50% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

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[28] Shunk and Wilds, *J. Amer. Chem. Soc.*, 1949, **71**, 3946.

(8) 3 : 5 : 5-Trimethyl*cyclo*hex-2-enol (10 g.), catalyst (0·25 g.), methanol (10 ml.), 20°/16 hr. Product: m. p. 49°, contained 20% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(9) 2-Methyl*cyclo*hexanone (25 g.), catalyst (2·5 g.), methanol (2 ml.), 20°. Product: d_4^{30} 0·9244 (containing 0·3% of ketone), contained 70% of *cis*-2-methyl*cyclo*hexanol.

(10) *o*-Cresol (20 g.), catalyst (0·5 g.), 160°. Product: d_4^{30} 0·9206, contained 32% of *cis*-2-methyl*cyclo*hexanol (ketone absent).

(11) *m*-Cresol (20 g.), catalyst (0·5 g.), 160°. Product: d_4^{30} 0·9101, contained 55% of *cis*-3-methyl*cyclo*hexanol (ketone absent).

(12) *p*-Cresol (600 g.), catalyst (30 g.), 160°. Product: d_4^{30} 0·9090, contained 63% of *trans*-4-methyl*cyclo*hexanol (ketone absent).

Atmospheric Reductions.—The compound to be reduced, dissolved in the relevant solvent with the stated amount of Adams platinum catalyst, was hydrogenated at 20° and atmospheric pressure. The solution was removed by decantation. When acids had been added these were removed by washing the products in light petroleum with alkali and water, removing the light petroleum, and totally distilling the final product.

The following compounds were reduced by this method with the results given:

(1) Dihydro*iso*phorone (5 g.), catalyst (1 g.), acetic acid (5 ml.). Product: m. p. 50·5°, contained 18% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(2) Dihydro*iso*phorone (5 g.), catalyst (1 g.), methanol (5 ml.). Product: m. p. 55·5°, contained 9% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(3) Dihydro*iso*phorone (5 g.), catalyst (0·4 g.), methanol (5 ml.), dimethyl*cyclo*hexylamine (1 drop). Product: m. p. 55°, contained 10% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(4) Dihydro*iso*phorone (10 g.), catalyst (1 g.), concentrated hydrochloric acid (10 ml.), water (10 ml.), light petroleum (5 drops). Product: m. p. 46·0° (containing 3·2% of dihydro*iso*phorone), contained 21% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(5) 4-*cyclo*Hexyl*cyclo*hexanone (5 g.), catalyst (2 g.), acetic acid (10 ml.). Product: m. p. 90·5° (containing < 1% of ketone), contained 54% of *cis*-4-*cyclo*hexyl*cyclo*hexanol.

(6) 4-*cyclo*Hexyl*cyclo*hexanone (5 g.), catalyst (2 g.), methanol (10 ml.). Product: m. p. 90·2° (containing < 0·5% of ketone), contained 55% of *cis*-4-*cyclo*hexyl*cyclo*hexanol.

(7) 2-Methyl*cyclo*hexanone (10 g.), catalyst (1 g.), acetic acid (10 ml.). Product: d_4^{30} 0·9244, contained 70% of *cis*-3-methyl*cyclo*hexanol (ketone absent).

(8) 3-Methyl*cyclo*hexanone (10 g.), catalyst (1 g.), acetic acid (10 ml.). Product: d_4^{30} 0·9088, contained 73% of *cis*-3-methyl*cyclo*hexanol (ketone absent).

(9) 4-Methyl*cyclo*hexanone (10 g.), catalyst (1 g.), acetic acid (10 ml.). Product: d_4^{30} 0·9101, contained 46% of *cis*-4-methyl*cyclo*hexanol (free from ketone).

(10) 4-Methyl*cyclo*hexanone (10 g.), catalyst (1 g.), methanol (10 ml.). Product: d_4^{30} 0·9075, contained 26% of *cis*-4-methyl*cyclo*hexanol (ketone absent).

Isomerisations.—The alcohol and catalyst, together with a solvent when the alcohol was solid at the working temperature, were shaken in an atmosphere of hydrogen at 100 lb. The total product was recovered and distilled.

(a) *With nickel.* At 130° (5 hr.). 3 : 3 : 5-Trimethyl*cyclo*hexanol (25 g. containing 90% of *trans*-isomer) and catalyst (0·5 g.) gave a product, m. p. 29·1°, containing 76% of *cis*-3 : 3 : 5-trimethyl*cyclo*hexanol and no ketone.

Experiments shown in Table 2 were carried out similarly. Also 3-methyl*cyclo*hexanol (50 g., containing 68% of *trans*-isomer) and catalyst (1·25 g.) at 160°/5 hr. gave a product, d_4^{30} 0·9083, containing 83% of *cis*-3-methyl*cyclo*hexanol and no ketone; and trans-4-*cyclo*hexyl*cyclo*hexanol (10 g.) and catalyst (0·5 g.) at 130°/5 hr. gave a product, m. p. 90·5—91·5°, containing 46—49% of *trans*-4-*cyclo*hexyl*cyclo*hexanol and no ketone.

(b) *With platinum.* (1) 3 : 3 : 5-Trimethyl*cyclo*hexanol (20 g., containing 89% of *trans*-isomer) and catalyst (1 g.) at 140°/5 hr. gave a product, m. p. 50·5°, containing 82% of *trans*-3 : 3 : 5-trimethyl*cyclo*hexanol.

(2) 3 : 3 : 5-Trimethyl*cyclo*hexanol (20 g., containing 89% of *trans*-isomer), catalyst (1 g.), and sodium carbonate (0·1 ml. of 10% aqueous solution) at 140°/5 hr. gave a product, m. p. 41°, containing 69·5% of *trans*-3 : 3 : 5-trimethyl*cyclo*hexanol (ketone absent).

(3) *trans*-4-*cyclo*Hexyl*cyclo*hexanol (20 g.) and catalyst (1 g.) at 160°/5 hr. gave a product, m. p. 91·4°, containing 49% of *trans*-4-*cyclo*hexyl*cyclo*hexanol (ketone absent).

Dehydrogenations with Nickel and Platinum.—(*a*) 3 : 3 : 5-Trimethyl*cyclo*hexanol (20 g.; mixed isomers) was refluxed with nickel (0·4 g.) in hydrogen for 16 hr. The product contained 61% of dihydro*iso*phorone.

(*b*) *cyclo*Hexanol (5 g.) and freshly prepared Adams platinum catalyst (2 g.) were refluxed in hydrogen for 1 hr. The solution was then decanted and washed twice with methanol (10, 5 ml.). Analysis showed 20% conversion into *cyclo*hexanone.

(*c*) *cyclo*Hexanol (5 g.) and Adams catalyst (1 g.) washed with acetic acid were treated as described above. Analysis showed 2·5% conversion into *cyclo*hexanone.

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